hydrogen migration in these photochemical processes occurs as a discrete step.[17,18] Our finding suggests that hydrogen migration under electron impact occurs similarly as a discrete primary step, which may be followed by a choice of possible secondary steps.[19]

The data presented in Table II were obtained with 70-eV electrons on an A.E.I. Model MS9 instrument with the source and inlet system at 250 and 100°, respectively, and the multiplier at high gain.[20]

Acknowledgment. This work was supported in part by U. S. Public Health Service Grant FR4378, National Institutes of Health Program Grant GM-16492, and National Science Foundation Grant BG 7866.

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(18) P. J. Wagner, *J. Amer. Chem. Soc.*, **89**, 5898 (1967); P. J. Wagner and G. S. Hammond, *Advan. Photochem.*, **5**, 21 (1968); J. N. Pitts, D. R. Burley, J. C. Mani, and A. D. Broadbent, *J. Amer. Chem. Soc.*, **90**, 5900 (1968); J. A. Barltrop and J. D. Coyle, *Tetrahedron Letters*, 3235 (1968).

(19) For opposing views, based on molecular orbital calculations, on the stepwise *vs.* concerted nature of the process comprising γ-hydrogen migration and β cleavage, see F. P. Boer, T. W. Shannon, and F. W. McLafferty, *J. Amer. Chem. Soc.*, **90**, 7239 (1968); R. C. Dougherty, *ibid.*, **90**, 5780 (1968).

(20) Following submission of this communication for publication, we learned of a similar study of the mass spectra of variously deuterated hexanals and heptanals by R. J. Liedtke and C. Djerassi, whose results are generally in good agreement with ours. We thank Drs. Liedtke and Djerassi for making their findings available to us before publication (R. J. Liedtke and C. Djerassi, *ibid.*, **91**, 6814 (1969)).

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High *exo*:*endo* Rate Ratios in the Solvolysis of the 2-Methyl- and 2-Phenyl-*exo*-5,6-trimethylene-2-norbornyl *p*-Nitrobenzoates. Evidence for the Unimportance of σ Participation in the High *exo*:*endo* Rate Ratios in Tertiary Norbornyl Derivatives

Sir:

A major difficulty in resolving the question of the factors responsible for the high *exo*:*endo* rate and product ratios in the solvolysis of 2-norbornyl derivatives[1] has been the problem of defining norbornyl systems in which σ participation cannot be a significant factor. An examination of the *exo*:*endo* rate and product ratios in such systems would soon establish whether such high ratios were simply steric properties of the norbornyl structure or were properties of σ participation.

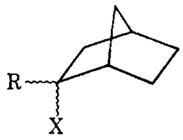
Several approaches have been employed. We have examined the properties of 2-norbornyl derivatives containing stabilizing substituents, such as *p*-anisyl, at the 2 position.[1,2] The argument is that a tertiary benzylic cation, especially one stabilized by a *p*-anisyl group, would make little demand on a neighboring saturated carbon–carbon bond for further stabilization.[3]

A second approach has been to introduce strongly electron-withdrawing substituents at the 7 position of the norbornyl system.[4] Such substituents should greatly reduce the ability of the C-1–C-6 carbon bond to donate electrons to the developing positive charge.

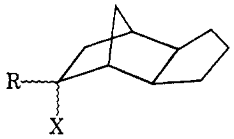
Another approach has been to bridge the *exo*-5,6[5] or the *exo*-4,5[6] positions of the norbornane structure by a trimethylene group. It is postulated that the increase in strain accompanying σ bridging will decrease σ participation as compared to the parent norbornyl system.

High *exo*:*endo* rate and product ratios are observed both for the highly stabilized tertiary norbornyl cations[2] and for the destabilized norbornyl derivatives carrying electron-withdrawing substituents in the 7 position. Both results indicate that σ participation cannot be a major factor in the high *exo*:*endo* rate and product ratios of normal norbornyl derivatives. On the other hand, low *exo*:*endo* rate ratios are observed for *exo*-5,6- and *exo*-4,5-trimethylene-2-norbornyl tosylates[7] and have been interpreted as indicating that σ participation cannot be an important factor in this system, but must be responsible for the high *exo*:*endo* rate ratio observed in the parent system.

This question will be considered later. However, the conclusion that the strain introduced by the trimethylene bridge acts to cancel σ participation would appear to make available norbornyl systems where such participation should not be a significant factor in the behavior of the compounds. Accordingly, we undertook to synthesize and to determine the rates of solvolysis of the epimeric 2-methyl- (II-Me) and 2-phenyl-*exo*-5,6-trimethylene-2-norbornyl *p*-nitrobenzoates (II-Ph) for comparison with the parent system (I-Me, I-Ph).



I, R = Me, Ph



II, R = Me, Ph

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(1) H. C. Brown, *Chem. Brit.*, **2**, 199 (1966).

(2) H. C. Brown and K. Takeuchi, *J. Am. Chem. Soc.*, **90**, 2691, 2693, 5268, 5270 (1968).

(3) For example, a *p*-anisyl group in the 7 position effectively cancels out the 10^{11} rate acceleration observed in the *anti*-7-dehydronorbornenyl system: P. G. Gassman, J. Zeller, and J. T. Lumb, *Chem. Commun.*, 69 (1968); P. G. Gassman and A. F. Fentiman, Jr., *J. Am. Chem. Soc.*, **91**, 1545 (1969).

(4) P. G. Gassman and J. M. Hornback, *ibid.*, **91**, 4280 (1969); P. G. Gassman, J. L. Marshall, J. G. Macmillan, and J. M. Hornback, *ibid.*, **91**, 4282 (1969).

(5) (a) R. S. Barnes, Ph.D. Thesis, Harvard University, 1951; (b) P. von R. Schleyer, Ph.D. Thesis, Harvard University, 1955; (c) K. Takeuchi, T. Oshika, and Y. Koga, *Bull. Chem. Soc. Japan*, **38**, 1318 (1965).

(6) E. J. Corey and R. S. Glass, *J. Am. Chem. Soc.*, **89**, 2600 (1967).

(7) The titrimetric *exo*:*endo* rate ratios for acetolysis at 25° is 11.2 for the 5,6[5c] and 8.6 for the 4,5[6] systems, as compared to 280 for the parent norbornyl system. The *exo*:*endo* rate ratio in secondary 2-norbornyl systems has also been reduced by strong carbonium ion stabilizing groups (an exocyclic double bond or cyclopropane ring) at C-3 (C. F. Wilcox, Jr., and R. G. Jesaites, *Tetrahedron Letters*, 2567 (1967); *Chem. Commun.*, 1046 (1967)). However, the *exo*:*endo* product ratio for the 3-methylene-2-norbornyl system is claimed to be very high (C. W. Jefford and W. Wojnarowski, *ibid.*, 129 (1968)), and this discrepancy between rate and product data has not yet been reconciled.

Table I. Rates of Solvolysis of Tertiary 2-Norbornyl and *exo*-5,6-Trimethylene-2-norbornyl Derivatives[a]

Compd	Isomer	Temp, °C	Rate constant, $k \times 10^6$ sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	Rel rate[b]	*exo*:*endo*
I-Me	*exo*-Cl[c]	25.0	30.2			1.00	
II-Me	*exo*-Cl	25.0	15.7	21.3	−9.4	0.52	
		50.0	274				
I-Ph	*exo*-Cl[d]	25.0	158,000			1.00	
II-Ph	*exo*-Cl	25.0	94,000[e]	17.6	−4.3	0.60	
		0.0	5,970				
		−10.5	1,565				
I-Me	*exo*-OPNB[f]	25.0	1.00×10^{-2}	26.3	−7.0	1.00	885
I-Me	*endo*-OPNB[f]	25.0	1.13×10^{-5}	30.2	−7.5	1.00	
II-Me	*exo*-OPNB[g]	25.0	3.00×10^{-3e}	27.9	−4.2	0.30	420
		100.0	48.9				
		125.0	552				
II-Me	*endo*-OPNB[h]	25.0	7.14×10^{-6e}	30.8	−6.0	0.63	
		125.0	4.69				
		150.0	49.8				
I-Ph	*exo*-OPNB	25.0	7.56	23.6	−2.8	1.00	143
		50.0	179				
I-Ph	*endo*-OPNB	25.0	5.3×10^{-2}	25.0	−7.7	1.00	
		75.0	30.2				
		100.0	364				
II-Ph	*exo*-OPNB[i]	25.0	4.24	24.2	−1.8	0.56	118
		50.0	109				
II-Ph	*endo*-OPNB[j]	25.0	3.6×10^{-2e}	26.3	−4.5	0.68	
		75.0	24.6				
		100.0	337				

[a] The tertiary chlorides were solvolyzed in absolute ethanol and the *p*-nitrobenzoates in 80% aqueous acetone. [b] 2-Norbornyl = 1.00. [c] H. C. Brown and F. J. Chloupek, *J. Am. Chem. Soc.*, **85**, 2322 (1963). [d] H. C. Brown, F. J. Chloupek, and M.-H. Rei, *ibid.*, **86**, 1248 (1964). [e] Calculated from data at other temperatures. [f] Reference 10b. [g] Mp 114.5–115.0°. [h] Mp 130.0–130.5°. [i] Mp 127° dec. [j] Mp 153–154° dec.

Clearly, if the strained trimethylene bridge causes σ participation to be relatively unimportant in the secondary derivatives, it should be even less significant in the stabilized tertiary derivatives.

Addition of methylmagnesium iodide and phenylmagnesium bromide to 5,6-*exo*-trimethylene-2-norbornanone gave the tertiary *endo* alcohols (II-Me-*endo*-OH, mp 81.5–82.0°; II-Ph-*endo*-OH, mp 73.4–74.6°). The alcohols were converted into the tertiary chlorides in the automatic hydrochlorinator.[8] Solvolysis of the chlorides in 60% aqueous acetone containing excess potassium bicarbonate yielded the corresponding *exo* alcohols (II-Me-*exo*-OH, mp 77.2–77.8°; II-Ph-*exo*-OH, mp 94.5–95.2°). The *p*-nitrobenzoates were prepared and their solvolysis carried out in 80% aqueous acetone. The *exo* chlorides were solvolyzed in absolute ethanol. The results are summarized in Table I.

The data reveal that the *exo*-5,6-trimethylene derivatives undergo solvolysis at slightly reduced rates as compared to the parent norbornyl compounds. However, the factor is quite small, within the range 0.3 to 0.7. Moreover, the *exo*:*endo* rate ratios are high, 420 for the 2-methyl and 118 for the 2-phenyl, easily comparable with those exhibited by the parent norbornyl system.

Equilibration[9] of II-Me-OH gave an *exo*:*endo* ratio at equilibrium of 1.2 at 25°. In other words there is almost no difference in the ground-state energies.

The data permit construction of a free-energy diagram for the solvolysis of the methyl derivatives (Figure 1).

It should be noted that there is a difference in energy of the two transition states of 3.6 kcal/mole. To what can this be attributed? If σ participation is unimportant in such strained secondary derivatives,[5] it surely cannot be significant in these more stable tertiary derivatives. It appears possible to account for this phenomenon only in terms of the changes in steric strain in approaching the respective transition states[10] (III, IV).

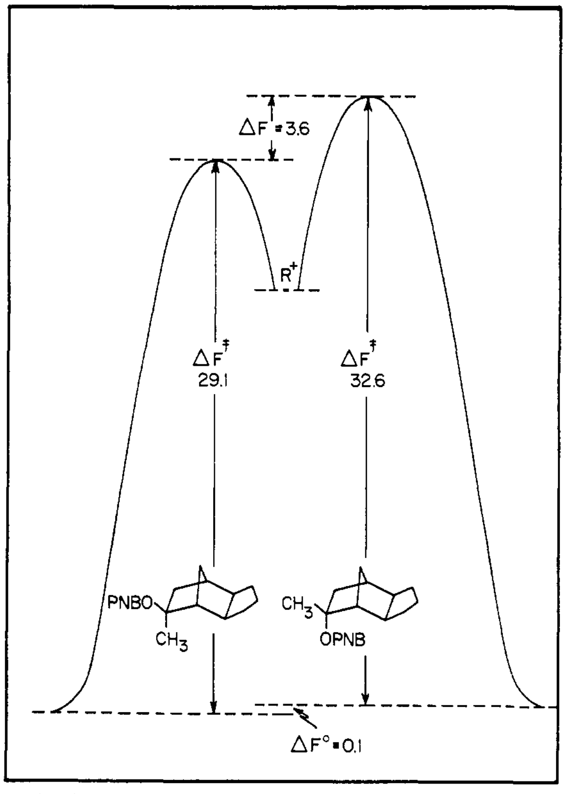

Figure 1. Free energy diagram for the solvolysis of the 2-methyl-*exo*-5,5-trimethylene-2-norbornyl *p*-nitrobenzoates in 80% aqueous acetone at 25° (all numbers in kcal/mole).

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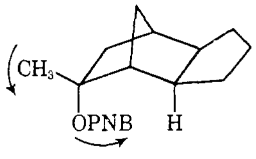
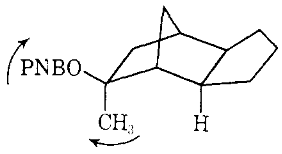
(8) H. C. Brown and M.-H. Rei, *J. Org. Chem.*, 31, 1090 (1966).

(9) M.-H. Rei and H. C. Brown, *J. Am. Chem. Soc.*, **88**, 5335 (1966).



III



IV

The present results make it quite clear that high *exo*:*endo* rate ratios can be observed in norbornyl derivatives where σ participation is not a factor. The problem remains: what is the factor responsible for the low *exo*:*endo* rate ratios in the secondary 5,6- and 4,5-*exo*-trimethylene-2-norbornyl derivatives?[11] We hope to examine this question experimentally.

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(10) (a) H. C. Brown and S. Ikegami, *J. Am. Chem. Soc.*, **90**, 7122 (1968); (b) S. Ikegami, D. L. Vander Jagt, and H. C. Brown, *ibid.*, **90**, 7124 (1968).

(11) In the parent norbornyl system, the secondary and tertiary derivatives exhibit very similar behavior. There is a natural reluctance to ascribe such similar behavior to totally different causes. However, we must not overlook the possibility that this may be the case. It is highly important for the theory of solvolysis to attain an understanding of the reason for the low *exo*:*endo* rate ratio in the trimethylene derivatives. It may turn out that this is indeed the result of decreased σ participation. However, caution must be exercised here also. The theory of σ participation is still in an exceedingly qualitative stage. Thus, it was originally predicted that the introduction of methyl groups in the 6 position of norbornyl would result in enhanced σ participation and an enhanced rate. When a decreased rate was observed, it was argued that methyl substituents, for steric reasons, should hinder σ participation (P. von R. Schleyer, M. M. Donaldson, and W. E. Watts, *J. Am. Chem. Soc.*, **87**, 375 (1965)). Indeed, had the trimethylene derivatives exhibited an enhanced *exo*:*endo* rate ratio, the theory could have accommodated even this. It would merely have been argued that the strain had polarized the C-1–C-6 bond and caused it to be a better donor.

It is important to recognize that the 5,6-trimethylene bridge may have important effects on reactivity other than its postulated influence on σ participation. For example, we have observed that the hydroboration of *exo*-5,6-trimethylenenorbornene yields an *exo*:*endo* product ratio of 10, whereas norbornene exhibits a product ratio of 200. These results are remarkably similar to the *exo*:*endo* rate ratios for the tosylates in the two systems, 11.2 and 280, respectively. Consequently, it is essential that we exercise caution as we grope our way to a better understanding of the chemical behavior of these fascinating rigid polycyclic systems.

(12) National Science Foundation Cooperative Fellow, 1965–1967; Ph.D. Thesis, Purdue University, 1967.

(13) National Science Foundation Predoctoral Fellow, 1963–1964; Ph.D. Thesis, Princeton University, 1964.

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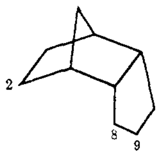
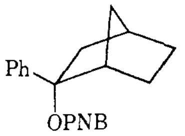
Evidence for Steric Hindrance to Ionization in the Slow Rates of Solvolysis of the Tertiary 2-, 8-, and 9-Phenyl-*endo*-5,6-trimethylene-*endo*-norbornanyl *p*-Nitrobenzoates. An Unusually High *exo*:*endo* Rate Ratio Not Involving σ Participation

Sir:

The U-shaped structure of the *endo*-5,6-trimethylenenorbornane system (I) appears ideal for the investigation of the possible role of steric hindrance to ionization as a major factor in the rates of solvolysis of bicyclic derivatives.[1,2] Accordingly we undertook to synthesize the tertiary 2-, 8-, and 9-phenyl *p*-nitrobenzoate derivatives (V, VI, VII) and to run their rates of solvolysis in 80% aqueous acetone for comparison with appropriate models (II, III, IV). We also synthesized the *exo* isomer VIII to obtain the *exo*:*endo* rate ratio.

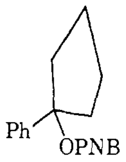


I



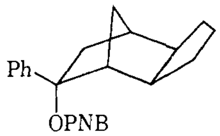
II

$^{1}/_{45}$



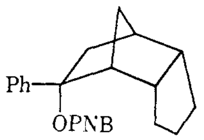
III

1.00



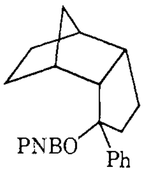
IV

$^{1}/_{63}$



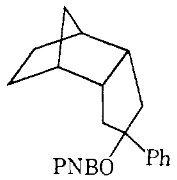
V

$^{1}/_{1030}$



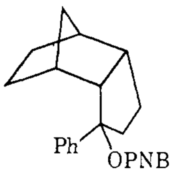
VI

$^{1}/_{1900}$



VII

$^{1}/_{27}$



VIII

6.1

exo:*endo* = 11,600

Addition of phenylmagnesium bromide to 5,6-*endo*-trimethylene-2-norbornanone gave the tertiary *endo* alcohol V-OH, mp 94.7–95.0°. Similarly, the corresponding 8- and 9-norbornanones were converted into the corresponding tertiary alcohols VI-OH, mp 91.5–92.3°; VII-OH, mp 93.5–94.5°. Treatment of VI-OH with hydrogen chloride gave the olefin instead of the chloride. The olefin was epoxidized[3] and the crude unstable epoxide reduced with lithium aluminum hydride to give the *exo*-8-ol, VIII-OH, mp 118.2–118.8°.[4] The rate data are summarized in Table I.

If we consider the 1-phenylcyclopentyl system to constitute a reasonable model for these derivatives, it is apparent that all of the *endo* isomers solvolyze at greatly reduced rates compared to the model. Thus II solvolyzes at $^{1}/_{45}$ and IV at $^{1}/_{63}$ the rate of III. It should be noted that there is little difference between II and IV. However, if the 5,6-trimethylene bridge is made *endo*, as in V, the relative rate decreases sharply to $^{1}/_{1030}$. Presumably this is a reflection of the greater steric hindrance to ionization afforded the *p*-nitrobenzoate moiety by the *endo*-trimethylene bridge as compared to the *exo*.

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(1) H. C. Brown, I. Rothberg, P. von R. Schleyer, M. M. Donaldson, and J. J. Harper, *Proc. Natl. Acad. Sci. U. S.*, **56**, 1653 (1966).

(2) H. C. Brown, W. J. Hammar, J. H. Kawakami, J. Rothberg, and D. L. Vander Jagt, *J. Am. Chem. Soc.*, **89**, 6378 (1967).

(3) G. B. Payne, *Tetrahedron*, **18**, 763 (1962).

(4) All compounds exhibited ir and pmr spectra and analytical data in agreement with the assigned structures.